Process for producing an Si_3N_4-coated SiO_2 shaped body

The invention relates to a process for producing an Si_3N_4-coated SiO_2 shaped body.

Porous, open-pore, amorphous SiO_2 shaped bodies are used in numerous technical fields. Examples which may be mentioned include filter materials, thermal insulation materials or heat shields. Furthermore, porous, open-pore, amorphous SiO_2 shaped bodies in rectangular form are used to crystallize silicon in the production of polycrystalline solar silicon ingots. These rectangular crucibles are referred to below as solar crucibles.

If liquid silicon is crystallized through slow cooling in the solar crucibles, it shrinks to a greater extent than the solar crucible made from SiO_2. Since the silicon is very securely joined to the inner side of the crucible, cracks occur in the polycrystalline silicon ingot. Since this must be avoided under all circumstances, all solar crucibles are provided on the inner side with a layer of Si_3N_4, which prevents the silicon from bonding to the crucible.

The porous, open-pore, amorphous solar crucibles are generally produced using a ceramic slip casting process. In this process SiO_2 particles are dispersed in water, are shaped, for example by means of a pressure die-casting process and are then dried and consolidated (partially sintered) by means of a heat treatment (sintering). In a second step, the Si_3N_4 layer is applied to the inner side. The prior art in this context is represented by the use of Si_3N_4 powder applied to the crucible surface using a plasma process, known as plasma spraying, where it forms the Si_3N_4 layer.

To maximize the efficiency of the solar silicon, it is extremely important for the high-purity silicon not to be

contaminated with metals during the crystallization. Therefore, both the solar crucible and the Si_3N_4 layer have to be produced in as pure a form as possible.

In the methods for sintering the porous, open-pore, amorphous solar crucibles which are known from the prior art, such as, for example, furnace sintering, zone sintering, arc sintering, contact sintering, sintering with hot gases or by means of plasma, the solar crucibles that are to be sintered are heated by the transfer of thermal energy or thermal radiation. If the solar crucibles to be produced by this route are to have an extremely high purity with regard to any type of foreign atoms, the use of hot gases or hot contact surfaces leads to undesired contamination with foreign atoms.

If the Si_3N_4 layer is applied by means of a plasma process, thermal energy is likewise transferred by means of thermal radiation. In this case too, the use of hot gases leads to undesired contamination with foreign atoms.

Furthermore, the prior art has disclosed complex two-stage processes for producing Si_3N_4-coated solar crucibles.

It is an object of the present invention to provide a process for producing Si_3N_4-coated SiO_2 shaped bodies in which the risk of contamination to both the Si_3N_4 layer and the SiO_2 shaped body is reduced.

This object is achieved by a process in which a precursor which is suitable for forming an Si_3N_4 sintered layer is applied to the surface of an amorphous, open-pore SiO_2 green body, and then this surface of the SiO_2 green body is heated by contactless heating by means of a laser beam, in such a manner that the precursor is converted in situ into an Si_3N_4 sintered layer

under a laser beam.

In principle, it is possible to use all types of lasers, but it
is preferable to use a laser with a beam with a wavelength of
10.6 μm. In particular, all commercially available CO_2 lasers
are suitable for use as the laser.

An SiO_2 green body is to be understood as meaning a porous,
amorphous, open-pore shaped body produced from amorphous SiO_2
particles (silica glass) by shaping steps. The green body has
preferably not yet been subjected to consolidation by means of
a heat treatment.

SiO_2 green bodies are known from the prior art. Their production
is described, for example, in patents EP 705797, EP 318100,
EP 653381, DE-A 2218766, GB-B-2329893, JP 5294610,
US-A-4,929,579. SiO_2 green bodies, whose production is described
in DE-A1-19943103, are particularly suitable.

All materials which, after heating, are able to form an Si_3N_4
sintered layer can be used as precursors for forming the Si_3N_4
layer. Examples of these materials include Si_3N_4 powder, silicon
powder, silicon oxide/carbon mixtures or polysilazanes. If the
shaped body according to the invention is a solar crucible, it
is preferable for the precursor to be applied on one side, to
the inner-side surface of the SiO_2 green body.

The preferred precursor is an Si_3N_4 powder. It is applied to the
surface of the green body, dried if appropriate, and then forms
an Si_3N_4 sintered layer as a result of the laser beam energy
which is adsorbed.

All commercially available powders (for example those produced
by H.C. Stark) can be used as the Si_3N_4 powder. Particularly

fine-grained Si_3N_4 powders with a grain size of between 100 nm
and 100 μm, are preferably used, particularly preferably those
with a grain size of between 100 nm and 50 μm, and very
particularly preferably those with a grain size of between
100 nm and 10 μm.

The Si_3N_4 powder can be applied to the surface of the SiO_2 green
body using all methods known to the person skilled in the art.
It is preferable for the surface to be sprayed with an Si_3N_4
powder dispersion. Suitable dispersants are in principle all
solvents, and it is preferable to use alcohols, acetone and
water, with water being particularly preferred. Furthermore,
all additives which are known to the person skilled in the art,
such as for example dispersants and liquefiers, can be used to
improve the dispersion of the Si_3N_4 powder.

If the Si_3N_4 powder is applied as a dispersion, it is preferable
for the layer to be dried after it has been applied. The drying
is in this case carried out by means of methods known to the
person skilled in the art, such as for example vacuum drying,
drying by means of hot gases, such as for example nitrogen or
air, or contact drying. A combination of the individual drying
methods is also possible. Drying by means of hot gases is
preferred.

The Si_3N_4 powder layer obtained in this way generally has a
layer thickness of from 1 to 1000 μm, preferably a layer
thickness of from 1 to 500 μm and particularly preferably of
from 1 to 100 μm. Fig. 1 shows a correspondingly coated
surface.

To form the Si_3N_4 sintered layer and preferably to
simultaneously consolidate the green body by partial sintering,
the green body, after the precursor has been applied, is

irradiated by a laser beam with a focal spot diameter of
preferably at least 2 cm.

The irradiation is preferably carried out with a radiation
power density of from 50 W to 500 W per square centimeter,
particularly preferably from 100 to 200 and very particularly
preferably from 130 to 180 W/cm^2. The power per cm^2 must be at
least sufficient to form an Si_3N_4 sintered layer.
The formation of the Si_3N_4 sintered layer preferably takes place
at a temperature of between 1000°C and 1600°C, particularly
preferably between 1000°C and 1200°C.

The irradiation is preferably carried out uniformly and
continuously.

The uniform, continuous irradiation of the pretreated SiO_2 green
body can in principle be carried out through a movable laser
optic and/or a corresponding movement of the crucible in the
laser beam.

The movement of the laser beam can be carried out using all the
methods known to the person skilled in the art, for example by
means of a beam-guidance system which allows the laser focus to
move in all directions. The movement of the green body in the
laser beam can likewise be carried out using all methods known
to the person skilled in the art, for example by means of a
robot. Furthermore, a combination of the two movements is
possible.

In the case of relatively large shaped bodies, e.g. solar
crucibles, scanning, i.e. a continuous, surface-covering
displacement of the specimen beneath the laser focal spot, is
preferred.

The formation of the Si_3N_4 sintered layer is controlled at all locations by the introduction of laser power.

It is preferable for the Si_3N_4 sintered layer to be formed as uniformly as possible. On account of the geometry of the SiO_2 green body, it may be the case that the laser beam does not always impinge on the green-body surface at a constant angle during the irradiation of the green body. Since the absorption of the laser radiation is angle-dependent, this results in an Si_3N_4 sintered layer of uneven thickness. A uniform Si_3N_4 sintered layer is obtained by virtue of the fact that the temperature in the focal spot of the laser can be measured at any time using a suitable means for measuring the temperature of the focal spot. Some of the reflected thermal radiation is transmitted via a special mirror system to a pyrometer which is used for temperature measurement.

Incorporating this temperature measurement into the overall system of laser and moving green body furthermore allows one or more of the process variables laser power, displacement travel, displacement speed and laser focus to be adapted during the laser irradiation of the green body, in such a way that it is possible to produce a uniform Si_3N_4 sintered layer (Figs. 2 and 3).

Furthermore, it is important in the process according to the invention that the SiO_2 green bodies have a porous structure, so that it is easy for precursors to infiltrate into the region of the green body close to the surface. This allows the formation of a silicon oxynitride interface between the SiO_2 body and the Si_3N_4 sintered layer.

The formation of the Si_3N_4 sintered layer may preferably be carried out under a reduced pressure or vacuum throughout the

entire process.

If the process is carried out under a reduced pressure, the
pressure is below standard pressure of 1013.25 mbar, and is
particularly preferably between 0.01 and 100 mbar, very
particularly preferably between 0,01 and 1 mbar. In a preferred
embodiment, it is also possible to carry out the process
in vacuo ($< 10^{-3}$ mbar), in order to produce layers which are
completely free of bubbles.

The accurate residence time of the focal spot can be used to
control not only the Si_3N_4 sintered layer but also the
consolidation of the green body, through to complete
vitrification.
This is realized by thermal conduction from the hot surface of
the body into the shaped body at temperatures above 1000°C.

On account of the very low thermal conductivity of silica
glass, the process according to the invention can be used to
produce a very sharp, defined interface between consolidated
and unconsolidated regions in the SiO_2 shaped body. This leads
to SiO_2 shaped bodies with a defined sintering gradient.

Furthermore, the extreme temperature profile in the SiO_2 green
body during the process suppresses crystallization of the
silica glass.

Since in the case of inner-side consolidation of a green body
in crucible form, there is no shrinkage of the crucible outer
side, it is in this way easy to produce near net shape
crucibles.

The partially-sintered, open-pore SiO_2 shaped body provided with
an Si_3N_4 sintered layer on the inner side is preferably a

crucible for the crystallization of solar silicon.

Fig. 1 shows an SEM image of an SiO_2 green body coated with Si_3N_4 powder.

Fig. 2 shows an SEM image of an SiO_2 shaped body with an Si_3N_4 sintered layer after the process according to the invention has been carried out. Points at which the formation of sintered necks are visible are marked by arrows.

Fig. 3 shows the X-ray diffractometer spectrum (XRD) for an SiO_2 shaped body with an Si_3N_4 sintered layer after the process according to the invention has been carried out.

The invention is described in more detail below on the basis of examples.

Example 1: Production of an open-pore, porous, amorphous SiO_2 green body in crucible form

Production was based on the process described in US-A-2003-0104920.

3800 g of double-distilled H_2O were introduced into a 10 liter plastic tub. First of all, 712 g of fumed silica, BET surface area 200 m^2/g, obtainable under the trade name Wacker HDK® from Wacker Chemie GmbH. Munich, were stirred in over the course of 30 min using a plastic-coated propeller stirrer. Then, 8188 g of fused silica, mean particle size 15 μm, obtainable under the trade name Excelica® SE-15 from Tokuyama, were added in portions over the course of 30 min and dispersed.
Once dispersion was complete, the dispersion was subjected to a slight pressure reduction (0.8 bar) for 10 minutes in order to remove any included air bubbles.

The dispersion produced in this way consists of 8900 g of solid, corresponding to a solids content of 70% by weight (composed of 92% fused silica and 8% fumed silica).

The green body was produced by means of ceramic pressure die-casting. For this purpose, the SiO_2 dispersion from a storage container is forced under a pressure of 10 bar through a system of lines between two open-pore plastic membranes made from methyl methacrylate. The membranes have a porosity of 30% by volume and a mean pore radius of 20 μm. The distance between the two membranes allows the formation of a 10 mm thick body. The two membranes are subjected to a closure pressure of 200 bar.

The pressure acting on the dispersion forces the majority of the water in the dispersion into the membranes. The SiO_2 body is formed.

After the formation of the bodies, lasting 45 min, has ended, the pressure in the storage container is reduced to 0 bar above standard pressure. Special air and water lines laid in the membranes enable the shaped body formed to be acted on by air or water through the porous membranes for the purpose of final shaping. In the process, the shaped body is detached from the membrane.

The shaped body is detached firstly from the outer membrane and then from the inner membrane.

The amorphous, open-pore, porous shaped body produced in this way has a solids content of 89% by weight and a residual water content of 11% by weight. After drying for 3 hours at 90°C, the shaped body is completely dry.

Example 2: Inner-side coating with Si_3N_4 powder

172 g of Si_3N_4 powder (produced by H.C. Stark, D_{50} value 4 μm) were dispersed in 50 g of double-distilled water with the aid of a plastic-coated propeller stirrer. This dispersion was sprayed uniformly onto the inner side of the crucible, with the aid of a commercially available paint gun, until a 100 μm thick layer had formed (cf. Fig. 1). This was followed by drying for one hour at 90°C in a drying cabinet.

Example 3: Formation of the Si_3N_4 sintered layer by means of CO_2 laser

The crucible was irradiated with a radiation power of 3 kW by means of an ABB robot (IRB 2400 model) under the focus of a CO_2 laser (TLF 3000 Turbo model).

The laser was equipped with a rigid beam guidance system and all the degrees of freedom of the movement were provided by the robot. In addition to a diverter mirror, which diverts the radiation emerging horizontally from the laser resonator into the vertical, the beam guidance was also equipped with optics for widening the primary beam. The primary beam had a diameter of 16 mm. After the parallel primary beam had passed through the widening optics, a divergent beam path resulted. The focal spot on the crucible had a diameter of 50 mm, with a distance of approx. 450 mm between optics and crucible. The robot was controlled using a program matched to the crucible geometry. With the crucible rotating (angular velocity 0.15°/s), first of all the laser covered the upper edge of the crucible over an angle range of 375°. Then, the remainder of the inner surface of the crucible was covered by the laser on a helical path. The rotational speed and advance rate of the crucible on an axis from the edge of the crucible toward the center were in this case accelerated in such a way that the area covered per unit time was constant. The irradiation was carried out at 150 W/cm^2.

In the same process step, in addition to the formation of an Si_3N_4 sintered layer on the surface of the green body, the SiO_2 shaped body was also partially sintered as a result of heat conduction from the hot inner surface into the interior of the shaped body. After the laser irradiation, the crucible is covered over its entire surface with a 100 μm thick, uniform, solid Si_3N_4 sintered layer yet retained its original external geometry. (cf. Fig. 2)